Anionic Polymerization of Monomers Containing Functional Groups. 5.[1] Anionic Polymerizations of 2-, 3-, and 4-Cyanostyrene

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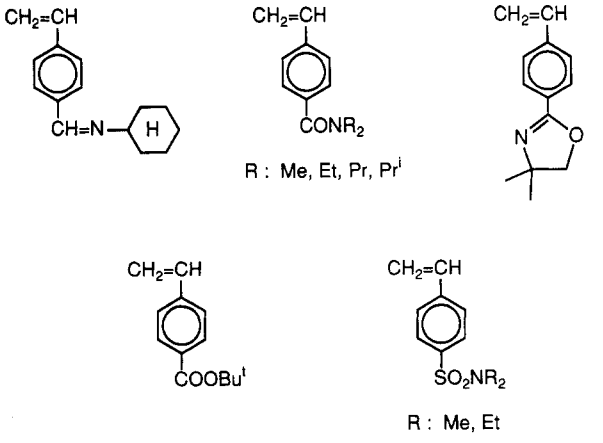
ABSTRACT: Anionic polymerizations of 4-cyanostyrene (1), 3-cyanostyrene (2), and 2-cyanostyrene (3) were carried out in tetrahydrofuran (THF). The initiators included lithium naphthalenide, potassium naphthalenide, oligo(α-methylstyryl)dilithium and -dipotassium, (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium, [1,1-bis[4′-(trimethylsilyl)phenyl]hexyl]lithium, and [1,1,4,4-tetrakis[4′-(trimethylsilyl)-phenyl]butanediyl]dipotassium. The polymerization of 1 proceeded quantitatively with each of these initiators at −78 °C for 30 min. The resulting polymers all possessed molecular weights predicted from the molar ratios of monomer to initiator and narrow molecular weight distributions (MWDs). The persistency of propagating activity at the chain end of poly(1) was confirmed by the quantitative initiation efficiency in the postpolymerization at −78 °C. These results strongly indicated that the anionic polymerization of 1 afforded a stable living polymer under the conditions. The Mark–Houwink equation for poly(1), $[\eta] = 1.004 \times 10^{-4}M^{0.749}$ (in *N,N*-dimethylformamide at 40 °C), was correlated. New block copolymers, poly(1-*b*-styrene-*b*-1) and poly(methyl methacrylate-*b*-1-*b*-methyl methacrylate), could be synthesized by using a living polymerization system of 1. The results of the polymerization of both 2 and 3 were not very satisfactory from the viewpoint of living polymerization. The polymerization of 2 did not occur at −78 °C at all but proceeded quantitatively with warming to −30 °C. However, undesirable side reactions might considerably occur at this temperature from the fact that the resulting poly(2) had a somewhat broad MWD. The anionic polymerization of 3 gave polymeric products having low molecular weights only in a 30% yield even for the longer reaction time of 200 h at −78 °C. The resulting poly(3)s were again found to have broad MWDs.

Introduction

We have recently studied the anionic polymerizations of a series of *para*-substituted styrenes containing the electron-withdrawing groups[2] *N*-alkylimino,[3] oxazolinyl,[4] *N,N*-dialkylamide,[5] *tert*-butyl ester,[6] and *N,N*-dialkylsulfonamide[7] (Chart I). The vinyl polymerizations of these monomers proceeded quantitatively, and the resulting polymers had predicted molecular weights based on the molar ratios of monomer to initiator and narrow molecular weight distributions (MWDs). The propagating carbanions at the chain ends maintained quantitative activities, promoting further polymerization to produce well-defined block copolymers after complete consumption of the monomers. These results clearly demonstrated that stable living polymers were produced in the polymerization reactions of these functional monomers. This is a surprising finding because these polar electron-withdrawing groups are usually believed to be susceptible to nucleophilc attack of the anionic initiators and the propagating chain end. Our success of the living polymerization of these monomers may be due to the stabilization of carbanions at their active chain ends by these electron-withdrawing groups. Furthermore, the extension of the π-conjugated system of the terminal benzylic carbanion[8] may also provide an additional effect to stabilize the propagating carbanion due to the resonance effect of the *para*-substituted electron-withdrawing groups. Thus, the electron-withdrawing group plays a very important role to yield the stable propagating chain end of the living polymer.

This success suggested the possible extension to styrenes with other electron-withdrawing groups. Here we choose the cyano group as an electron-withdrawing group for extension of our investigations concerning the anionic living polymerizations of functional styrenes. Since the cyano group is known to show a strong electron-withdrawing effect and involve a carbon–nitrogen triple bond

Chart I



containing a π-conjugated electron,[9] similar polymerization behavior may be expected in the polymerization of cyanostyrenes. In fact, in a preceding communication,[10] we found that the anionic polymerization of 4-cyanostyrene (1) proceeded well to afford a stable living polymer in THF at −78 °C. The resulting poly(1)s had controlled molecular weights and very narrow MWDs. The persistency of propagating activity of poly(1) was confirmed by the quantitative initiation efficiency in the postpolymerization. These results indicate that the cyano group of 1 may permit the anionic living polymerization possibly due to the stabilization of the propagating carbanion by the cyano group, similar to other electron-withdrawing groups.

In this paper, we report a detailed study of the anionic living polymerization of 1 under various conditions including the synthesis of block copolymer containing the poly(1) segment. We also examine the anionic polymerizations of two additional positional isomers of cyanostyrene, 3-cyanostyrene (2) and 2-cyanostyrene (3) (Chart

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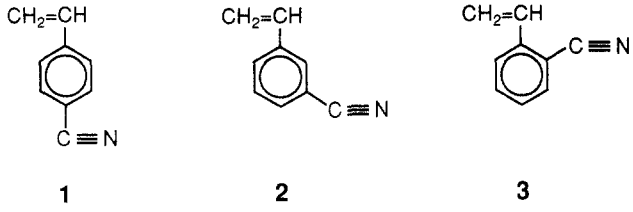
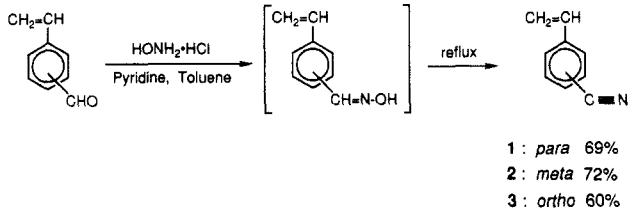
Chart II



1 2 3

Scheme I



1 : *para* 69%
2 : *meta* 72%
3 : *ortho* 60%

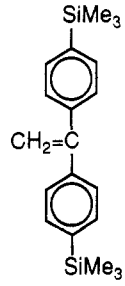
II), because it is expected that the position of the cyano group on the aromatic ring may affect their polymerization behaviors.

Results and Discussion

1. Syntheses of Cyanostyrenes. Cyanostyrenes were previously prepared by the coupling reaction of aryl bromide[11] or diazonium salt[12] and cuprous cyanide. Unfortunately, these synthetic methods involved the use of highly toxic cuprous cyanide, and the yields of products were moderate. We have developed an alternative method to synthesize cyanostyrenes by using a modified reaction reported by Saednya.[13] The reaction involves a one-pot synthesis of cyanostyrenes from the corresponding formylstyrenes, which proceeds via the formation of oxime in situ and the subsequent dehydration of the resulting oxime as shown in Scheme I. Yields of cyanostyrenes were usually fairly good in these two-step reactions. The resulting nitrile monomers were thoroughly purified by several fractional distillations over calcium hydride in vacuo. Then the monomers were finally distilled over phenylmagnesium chloride on the vacuum line to attain sufficient purity of monomers for the anionic polymerization.

2. Anionic Polymerization of 4-Cyanostyrene (1). As mentioned in the Introduction, the cyano group is a well-known electron-withdrawing group.[9] The strong electron-withdrawing nature is clear from the fact that the Hammett σ-value of the cyano group is estimated to be in the range of 0.64–0.70.[14] Reynolds et al.[15] reported that the substituent effects could be evaluated from the chemical shift of the β-carbon of the vinyl group in the ^{13}C NMR spectra of 4-substituted styrenes. In fact, the chemical shift of the vinyl β-carbon of 4-cyanostyrene (117.6 ppm) considerably shifts toward lower field from that of styrene (113.8 ppm).[16] The Hammett σ-value of the cyano group of 1 can also be estimated to be 0.75 from the chemical shift, which again suggests the strong electron-withdrawing character of the cyano group of 1. Accordingly, the electron-withdrawing cyano group may decrease the electron density of the vinyl group through the π-conjugated system, resulting in a high reactivity of 1 in the anionic polymerization. For example, Q and e values for 4-cyanostyrene are reported to be 1.67 and 0.325, respectively.[17] As expected, the positive e value for 1 (e = 0.33) clearly supports the low electron density of the vinyl group and the higher reactivity of 1 than that of styrene (e = −0.8) in the anionic polymerization. In addition to this, the extension of the π-conjugated system of the monomer molecule is apparent from the large Q value (Q = 1.67) compared with that of styrene (Q = 1.0). Thus, the strong electron-withdrawing effect of the cyano group will significantly influence the reactivities of cyanostyrenes in their polymerization reactions.

We first carried out the anionic polymerization of 1 in THF at −78 °C with [1,1-bis[4′-(trimethylsilyl)phenyl]-hexyl]lithium and [1,1,4,4-tetrakis[4′-(trimethylsilyl)-phenyl]butanediyl]dipotassium as initiators. These initiators were prepared at −78 °C in THF by the reactions of either *n*-butyllithium (*n*-BuLi)/heptane or potassium naphthalenide/THF and 1,1-bis[4′-(trimethylsilyl)phenyl]-ethylene (4).[10] On addition of 1 to the initiator solution,



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the color of the reaction mixture changed from rose red to dark red which resembles that of living polystyrene. The coloration was maintained during the course of polymerization until it was quenched with methanol. In some polymerization systems aiming at the syntheses of high molecular weight polymers, although the polymers precipitated as the reaction proceeded, 100% conversions of 1 were always attained in 20 h. The polymers were quantitatively obtained after precipitating the polymerization mixture in methanol. In the ^1H NMR spectrum of the resulting polymer, the signals corresponding to the vinyl protons of 1 completely disappear and broad signals due to the polymer backbone are observed. Typical ^{13}C NMR spectra of 1 and poly(1) are shown in Figure 1. After the polymerization, the signals corresponding to the vinyl carbons (117.6 and 135.2 ppm) completely disappear, and new signals corresponding to the methylene and methine carbons of the polymer main chain appear at 40–44 ppm. The signal due to the cyano carbon at 119.2 ppm is observed unchanged in the same region of the monomer. The infrared spectrum of the polymer exhibits the strong and characteristic C≡N stretching absorption at 2230 cm^{-1}, whereas the absorptions due to the vinyl deformation at 923 and 990 cm^{-1} no longer exist. These spectroscopic observations of the polymer suggest the expected structure of poly(1) obtained by the vinyl polymerization.

Table I summarizes the results of the anionic polymerization of 1. The molecular weights and MWDs of the poly(1)s were first measured by gel permeation chromatography (GPC) calibrated by standard polystyrenes using DMF as an eluent. All of the GPC curves of poly(1) showed sharp and unimodal peaks. The polydispersity indices ($\bar{M}_w/\bar{M}_n$) were within 1.1. However, the relative molecular weights of poly(1)s estimated from GPC calibration do not agree with the calculated values based on the molar ratio of monomer to initiator. They all present values approximately 3 times higher than the calculated ones. As discussed later, these deviations are probably due to the difference of hydrodynamic volume between poly(1) and polystyrene in DMF solution at 40 °C. The constancy of $\bar{M}_n$(GPC)/$\bar{M}_n$(calcd) over the whole range of molecular weights suggests the livingness of this polymerization

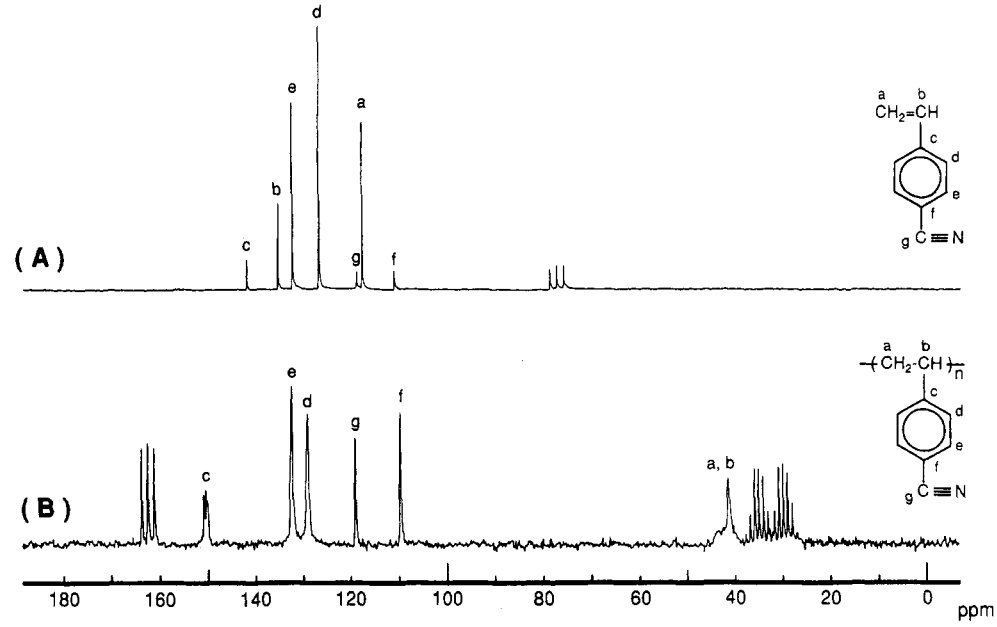


Figure 1. ^{13}C NMR spectra of 1 in $CDCl_3$ (A) and of poly(1) in DMF-d_7 (B).

Table I. Anionic Polymerization of 1 in THF at −78 °C for 1–20 h[a]

run	1, mmol	initiator, mmol	$10^{-3}\bar{M}_n$ calcd[b]	$10^{-3}\bar{M}_n$ NMR	$10^{-3}\bar{M}_n$ GPC[c]	$\bar{M}_w/\bar{M}_n$[d]	$10^{-3}\bar{M}_w$(LS)[e]
1	3.74	K-Naph,[f] 0.127/4, 0.172	8.2	8.7	23	1.07	
2	5.36	K-Naph, 0.117/4, 0.157	12	13	33	1.07	
3	7.01	K-Naph, 0.0970/4, 0.228	19	20	45	1.07	
4	9.85	*n*-BuLi, 0.0402/4, 0.0414	32	30	80	1.05	38
5	10.3	*n*-BuLi, 0.0453/4, 0.135	30	33	94	1.04	
6	11.6	*n*-BuLi, 0.0285/4, 0.0289	53	61	140	1.06	66
7	18.3	*n*-BuLi, 0.0239/4, 0.0244	99	122	270	1.09	137

[a] Yields of polymers were almost quantitative in each case. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of initiator; f = 1 or 2, corresponding to the functionality of the initiators. [c] $\bar{M}_n$(GPC) was obtained by GPC calibration using standard polystyrenes in DMF solution. [d] $\bar{M}_w/\bar{M}_n$ was estimated from GPC calibration for poly(1) as shown in eq 1. [e] $\bar{M}_w$(LS) was obtained by light scattering in DMF at 25 °C. [f] Potassium naphthalenide.

system, but a more accurate method for the determination of the molecular weights is necessary before any firm conclusion can be made.

In a preceding communication,[10] we employed an end-group analysis using ^1H NMR spectroscopy to estimate the molecular weights of the poly(1)s. For this purpose, we have synthesized novel anionic initiators containing trimethylsilyl protons as an NMR probe by the reaction of 4 and either *n*-BuLi or metal naphthalenides.[18] With these initiators, seven samples of poly(1) were prepared here. Comparing the relative integrated intensity between the trimethylsilyl protons and the aromatic or the methylene and methine protons of the poly(1) main chain, reproducible values of $\bar{M}_n$ were actually obtained within ±10%. These $\bar{M}_n$(NMR)s of the poly(1)s agree fairly well with the theoretical values predicted from the initial molar ratios of monomer to initiator as can be seen in Table I. Thus, the good agreement of the two values and the linear relationship between $\bar{M}_n$(NMR) and $\bar{M}_n$(GPC) give the following equation, which is useful to estimate the practical molecular weights of the poly(1) samples.

$$\bar{M}_n(\text{obsd}) = 0.459\bar{M}_n(\text{GPC}) - 3820 \quad (1)$$

The $\bar{M}_w/\bar{M}_n$ values were estimated by using the above calibration for poly(1), and the values are listed in Table I. These values are again within 1.1, which strongly indicate that all the polymers have narrow MWDs. In addition, the weight-average molecular weights of three poly(1) samples were independently determined by light scattering measurement. The values, $\bar{M}_w$(LS)s, are also listed in Table I. These absolute values of $\bar{M}_w$(LS)s are close to the weight-average molecular weights estimated from the $\bar{M}_n$(NMR)s and their MWDs by GPC. This closeness supports the reliability of the molecular weights obtained from the end-group analysis by ^1H NMR. Accordingly, these controlled molecular weights in the range of 8700–122 000 and narrow MWDs substantiate that the anionic polymerization of 1 is free from termination and transfer reactions, viz., the living character of the polymerization.

Effect of Anionic Initiator. We have performed the polymerization of 1 with various anionic initiators at −78 °C to examine the scope of the living system. The results are listed in Table II. The employed anionic initiators include lithium naphthalenide, potassium naphthalenide, (1,1-diphenylhexyl)lithium, cumylpotassium, oligo(α-methylstyryl)dilithium and -dipotassium, and (1,1,4,4-tetraphenylbutanediyl)dilithium and -dipotassium. With these initiators, the polymerizations of 1 quantitatively proceeded at −78 °C within 2 h. The molecular weights of the resulting poly(1)s were determined by using the above-mentioned GPC calibration curve. Every poly(1) thus obtained had a predictable molecular weight from the monomer to initiator ratio and very narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.05–1.09). Consequently, the anionic living polymerizations of 1 are also realized in these polymerization systems at −78 °C in THF. The initiators available for the living polymerization are widely ranging in chemical species (radical anion and carbanion), reactivities (metal naphthalenide and carbanions capped with α-methylsty-

Table II. Anionic Polymerization of 1 in THF[a]

run	1, mmol	temp (°C), time (h)	initiator, mmol	$10^{-3}\bar{M}_n$ calcd[b]	$10^{-3}\bar{M}_n$ obsd[c]	$\bar{M}_w/\bar{M}_n$[c]
8	3.98	−78, 2	*n*-BuLi, 0.0445	12	18	1.05
9	9.08	−78, 2	*n*-BuLi, 0.0946/DPE,[d] 0.177	13	14	1.05
4	9.85	−78, 20	*n*-BuLi, 0.0402/4, 0.0414	32	30	1.05
5	10.3	−78, 20	*n*-BuLi, 0.0453/4, 0.135	30	33	1.04
6	11.6	−78, 20	*n*-BuLi, 0.0285/4, 0.0289	53	61	1.06
7	18.3	−78, 20	*n*-BuLi, 0.0239/4, 0.0244	99	122	1.09
10	3.68	−78, 0.5	Li-Naph,[e] 0.0881	11	8.7	1.07
11	3.84	−78, 0.5	Li-Naph, 0.0844/α-MeSt,[f] 0.205	12	12	1.07
12	6.93	−78, 0.5	Li-Naph, 0.171/DPE, 0.234	11	11	1.07
13	9.37	−78, 2	Cumyl-K,[g] 0.0842/DPE, 0.131	15	15	1.09
14	7.97	−78, 2	Cumyl-K, 0.0427/DPE, 0.0705	24	27	1.06
15	9.15	−78, 12	Cumyl-K, 0.0281/DPE, 0.0407	42	37	1.07
16	3.79	−78, 0.5	K-Naph,[h] 0.0962	10	9.2	1.07
17	3.54	−78, 0.5	K-Naph, 0.0786/α-MeSt, 0.229	12	12	1.06
18	5.26	0, 1	K-Naph, 0.143/DPE, 0.201	9.9	11	1.49
19	3.84	−30, 1	K-Naph, 0.0991/DPE, 0.290	10	12	1.07
20	4.23	−78, 0.5	K-Naph, 0.102/DPE, 0.248	11	9.3	1.08
1	3.74	−78, 1	K-Naph, 0.127/4, 0.172	8.2	8.7	1.07
2	5.36	−78, 1	K-Naph, 0.117/4, 0.157	12	13	1.07
3	7.01	−78, 4	K-Naph, 0.0970/4, 0.228	19	20	1.07

[a] Yields of polymers were almost quantitative in each case. [b] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × *f*/[initiator] + MW of initiator; *f* = 1 or 2, corresponding to the functionality of the initiators. [c] $\bar{M}_n$(obsd) and $\bar{M}_w/\bar{M}_n$ were estimated from the GPC calibration using several poly(1) samples in DMF solution. [d] 1,1-Diphenylethylene. [e] Lithium naphthalenide. [f] α-Methylstyrene. [g] Cumylpotassium. [h] Potassium naphthalenide.

rene or 1,1-diphenylethylene), countercations (lithium and potassium), and functionalities (monofunctional and difunctional). Unfortunately, the poly(1) directly initiated with *n*-BuLi was found to have a molecular weight significantly higher than the predicted value, although its MWD was very narrow (run 8). We speculate that *n*-BuLi, a highly reactive nucleophile, may attack the cyano carbon of the monomer at the initiation step even at −78 °C to some extent. Then the decrease of concentration of the propagating carbanion at the initiation reaction increased the molecular weight of the resulting polymer but did not affect the MWD.

Effect of Polymerization Temperature. As described above, when we carried out the anionic polymerization of 1 at −78 °C, the MWDs of the resulting poly(1)s were narrow in all cases. When the polymerization temperature was raised to −30 °C, a polymer having a narrow MWD and predicted molecular weight was still obtained (run 19). By contrast, a broadening of the MWD ($\bar{M}_w/\bar{M}_n$ = 1.49) occurred when the polymerization was carried out at 0 °C. This is probably due to the undesirable side reaction of the propagating species during the course of the polymerization at temperatures over 0 °C. Nucleophilic attack of the propagating carbanion on the cyano groups might occur at this temperature. It should be mentioned that a suitable choice of the reaction temperature below 0 °C is necessary for complete control of the polymerization of 1.

Postpolymerization. Evidence for the living polymerization of 1 is also provided by the postpolymerization of 1 in THF at −78 °C. After 1 was completely polymerized with (1,1,4,4-tetraphenylbutanediyl)dilithium for 30 min, a second feed of 1 was added to the polymerization system. The mixture was allowed to stand for an additional 30 min to complete the second polymerization. The conversion of each polymerization was quantitative. The pre- and postpolymer possessed the molecular weights 7000 ($\bar{M}_w/\bar{M}_n$ = 1.04) and 16 000 ($\bar{M}_w/\bar{M}_n$ = 1.05), close to the respective theoretical values, 6800 and 16 000. It was found that the GPC curve of the prepolymer shifts toward that of the postpolymer on the higher molecular weight side, maintaining the sharp shape of the chromatogram (Figure 2). These results indicate that the active chain end of living poly(1) is stable at −78 °C at least for 30 min and is able to initiate further polymerization with quantitative efficiency. We have already ascertained that the propagating chain end of poly(1) containing potassium countercation is stable under identical conditions.[10] Accordingly, both lithium and potassium cation are able to promote the anionic living polymerization of 1.

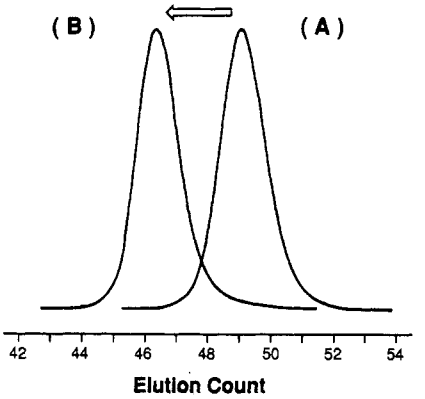


Figure 2. GPC curves of poly(1)s obtained at −78 °C: (A) the first-stage polymerization, $\bar{M}_n$(obsd) = 7000, $\bar{M}_w/\bar{M}_n$ = 1.04; (B) the second-stage polymerization, $\bar{M}_n$(obsd) = 16 000, $\bar{M}_w/\bar{M}_n$ = 1.05 (the second feed of monomer was added 30 min after the first-stage polymerization).

The results obtained here clearly demonstrate that the anionic living polymerization of 1 can be attained under various conditions. This success of living polymerization is a surprising fact judging from the numerous reports concerning the nucleophilic attack on the cyano group by carbanionic species similar to the initiators used here.[19]

3. Anionic Polymerization of 2-Cyanostyrene (3) and 3-Cyanostyrene (2). The results in the preceding section have clearly shown that the anionic polymerization of 4-cyanostyrene proceeded well to yield the stable living polymer under various conditions. In this section, we have carried out anionic polymerizations of the *ortho* and *meta* isomers (3 and 2) and found that the position of the cyano substituent strongly affects their polymerization behaviors. It is well known that the position of the substituent on the

Table III. Anionic Polymerization of 3 and 2 in THF

run	monomer, mmol	temp (°C), time (h)	initiator, mmol	yield, %	$10^{-3}\bar{M}_n$ calcd[a]	$10^{-3}\bar{M}_n$ obsd[b]	$\bar{M}_w/\bar{M}_n$[b]
21	3, 5.03	−78, 0.5	K-Naph,[c] 0.119/α-MeSt,[d] 0.306	17	2.5	2.7	1.32
22	3, 5.02	−78, 20	K-Naph, 0.113/DPE,[e] 0.119	15	2.1	6.5	1.42
23	3, 4.75	−78, 200	K-Naph, 0.121/DPE, 0.206	30	3.4	2.8	1.78
24	3, 4.83	−78, 20	Li-Naph,[f] 0.115/DPE, 0.192	8	1.2		
25	3, 4.94	−30, 3	K-Naph, 0.126/DPE, 0.210	11	1.5	2.4	1.29
26	2, 4.88	−78, 0.5	K-Naph, 0.116/4, 0.191	0			
27	2, 4.73	−78, 20	K-Naph, 0.139/DPE, 0.200	0			
28	2, 5.57	−78, 400	K-Naph, 0.124/DPE, 0.169	0			
29	2, 3.20	−78, 20	Li-Naph, 0.0843/4, 0.167	0			
30	2, 3.92	−30, 0.5	K-Naph, 0.0899/DPE, 0.178	27	3.4	2.7	1.06
31	2, 3.28	−30, 3	K-Naph, 0.106/DPE, 0.221	100	8.0	7.1	1.15
32	2, 6.09	−30, 20	K-Naph, 0.157/4, 0.272	100	10	11	1.16
33	2, 6.02	−30, 5	K-Naph, 0.0657/DPE, 0.215	40	9.6	11	1.16
34	2, 4.42	−30, 20	K-Naph, 0.0407/DPE, 0.139	100	28	24	1.19

[a] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2 × yield/[initiator] + MW of initiator. [b] $\bar{M}_n$(obsd) and $\bar{M}_w/\bar{M}_n$ were obtained by GPC calibration using standard polystyrenes in THF solution. [c] Potassium naphthalenide. [d] α-Methylstyrene. [e] 1,1-Diphenylethylene. [f] Lithium naphthalenide.

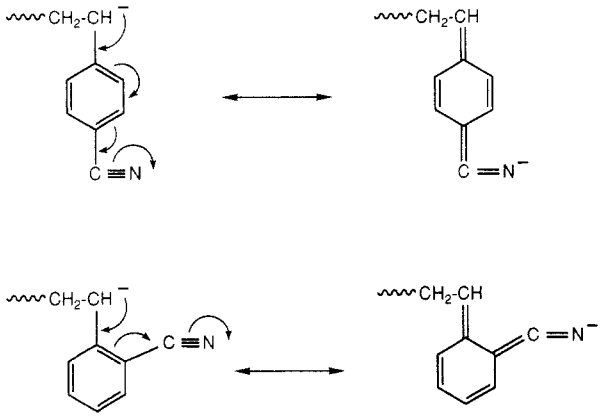
aromatic ring in organic aromatic compounds significantly influences the acidity, reactivity, and regioselectivity toward several reactions due to their electronic effects. If there is little or no steric effect of the substituent, the electronic substituent effects of the *para* and *ortho* isomers would be analogous to the situation found in organic reactions. This means that 2- and 4-cyanostyrene will promote similar polymerization behaviors. On the other hand, in the case of the *meta* isomer, only an inductive effect (no resonance effect) of the cyano group would be expected.

First, the anionic polymerization of the *ortho* isomer, **3**, was carried out under conditions identical to those used for the *para* isomer, **1**, (Table III). An immediate color change of the reaction mixture from dark red to bright red was observed at −78 °C on addition of **3** to the initiator solution, but the resulting red color faded within 1 min. Most of the unreacted monomer was recovered from the reaction system in each polymerization. Polymeric product was obtained in a low yield after the reaction solution was poured into methanol. ^{1}H NMR and GPC analyses ascertained that the methanol-insoluble part was a poly(**3**) with a low molecular weight and a broad MWD. Attempts to polymerize **3** both for a long time (run 23) and at a higher temperature (run 25) were not successful. Poly(**3**) with a broad MWD was produced at most in 30% yield even after 200 h at −78 °C with (1,1,4,4-tetraphenylbutanediyl)dipotassium. These findings indicate that the active chain end of the poly(**3**) produced may be unstable and that a side reaction occurs in the early stage of the polymerization. The susceptibility of the *ortho* isomer to the side reaction can be accounted for by an intramolecular side reaction, which includes nucleophilic attack of the propagating carbanion on the cyano group located near the carbanion.

Next, the polymerization of the *meta* isomer, **2**, was investigated under identical conditions (Table III). An immediate color change of the reaction mixture again took place on addition of **2** to (1,1,4,4-tetraphenylbutanediyl)-dipotassium at −78 °C. In this case, the mixture maintained the red coloration during the reaction, but the monomer was quantitatively recovered after 0.5–20 h. No polymerization of **2** was found to occur under the conditions where the quantitative polymerization of the *para* isomer was attained. Furthermore, no polymeric products were obtained at −78 °C even after 400 h. When the polymerization temperature was raised from −78 to −30 °C, the polymerization of **2** proceeded. The rate of polymerization seemed to be slow even at −30 °C from the fact that the yield of polymer was only 27% after 30 min. A longer time of 3 h was required for a quantitative conversion (run 31). The chemical structure of the resulting polymer was ascertained as the poly(**2**) produced by the vinyl addition from the analyses of NMR and IR spectra. No heterogeneous structure was observed within the range of our spectroscopic measurements. The molecular weights of the polymers estimated by GPC agreed fairly well with the values calculated from the ratios of consumed monomers to initiators. The MWD of the resulting polymer was unimodal and narrow when the polymerization was carried out for 30 min, although its molecular weight and yield were low (run 30). However, when we carried out the polymerization for a longer time, the MWDs became somewhat broader, particularly after the complete consumption of the monomer. Although $\bar{M}_w/\bar{M}_n$ values were within 1.2, a bimodal peak with a tailing on the low molecular weight side was observed in the GPC chromatogram (runs 31–34). These phenomena suggest that side reactions occur slowly during the course of the polymerization of **2** at −30 °C, whereas the polymerization proceeds quantitatively. The side reactions are probably due to inter- and intramolecular nucleophilic attacks of the propagating carbanion on the cyano functionality.

From the polymerization results of **1**–**3**, we could find that the position of the cyano group seriously affects their polymerization reactions. Only the *para* isomer is capable of anionic living polymerization. Undoubtedly, the propagating carbanion stabilized by the *para*-substituted electron-withdrawing cyano group greatly contributes to form the living polymer in the polymerization of **1**. In contrast to the *para* isomer, the *meta* and *ortho* isomers undergo undesirable side reactions in greater or lesser degree. As shown in Scheme II, in the cases of **1** and **3**, the cyano groups on the benzenoid system can accept negative charge and stabilize the benzylic carbanions through π-electron resonance. The inductive effect of the cyano group also tends to stabilize both propagating carbanions. Thus, a similar electronic effect promoting the stabilization will be expected in the polymerizations of the *para* and *ortho* isomers. However, in the case of the propagating terminal of the *ortho* isomer, since the cyano group was located near the reactive benzylic carbanion, intramolecular nucleophilic attack of the carbanion on the cyano group might occur at an early stage of the polymerization. This serious side reaction resulted in a low yield of poly(**3**) with a broad MWD. In the case of **2**,

Scheme II



the resonance effect of the cyano group is negligible, since the terminal benzylic carbanion of the *meta* isomer cannot conjugate with the cyano substituent. Only the inductive effect of the group contributes a stabilization of the active chain end. The stabilization seems not to be enough for achieving the living polymerization of the *meta* isomer. A considerable amount of termination reactions might occur during the polymerization, although we could obtain poly(2) in quantitative yield by allowing the reaction to proceed for a long time.

As mentioned in the Introduction, we have reported successful examples of anionic living polymerization of styrene derivatives *para*-substituted with some electron-withdrawing functionalities.[2-7] From the results obtained here, it seems that the success of the living polymerization of the *para* isomer does not always mean that the *meta* and *ortho* isomers will also undergo living polymerization. Therefore, investigations of the anionic polymerization of the *meta* and *ortho* isomers containing various functional groups are of interest and should be carefully carried out. The substituent effects of electron-withdrawing groups on the anionic polymerizations of styrene derivatives can be comprehensively discussed in the near future.

4. Block Copolymerization of 1 with Styrene and Methyl Methacrylate (MMA). Interest in block copolymers has recently increased because of their properties as an interfacial agent between incompatible homopolymers[20] as well as their ordered morphologies observed in bulk. The success of the living polymerization of 4-cyanostyrene opens the way to the controlled synthesis of novel block copolymers containing polar poly(1) segments.

First, the synthesis of triblock copolymer was demonstrated by the sequential addition of styrene and 1 with a difunctional initiator. Styrene was first polymerized with potassium naphthalenide in THF at −78 °C, and then 1 was added to the reaction mixture. Both the first and second polymerizations smoothly proceeded and the yields of polymers were quantitative. Figure 3 shows GPC curves of the starting polystyrene and the polymer obtained after the second polymerization. Obviously, the GPC curve of the polystyrene shifted toward the higher molecular weight region after addition of 1. The content of poly(1) segment in the resulting polymer agreed with the calculated values based on the molar ratio of both feed monomers from the analysis of ^{1}H NMR. As shown in Table IV, the resulting polymer had a controlled molecular weight in accord with the calculated value and a narrow MWD as well as homopolystyrene obtained at the first-stage polymerization. These findings suggest that the polymer is the expected ABA type triblock copolymer, poly(1-*b*-styrene-*b*-1), with a desirable chain structure.

Next, we attempted the synthesis of the triblock copolymer of 1 and styrene with a reversed sequence. In this case, styrene monomer was added to the living poly(1) produced with (1,1,4,4-tetraphenylbutanediyl)dipotassium. However, virtual homopoly(1) and the unreacted styrene monomer were quantitatively recovered from the reaction mixture after the reaction for 2 h in THF at −78 °C (Table IV, run 37). This means that the living poly(1) could not initiate the polymerization of styrene under the conditions. The contrasting results of the two block copolymerizations of 1 with styrene clearly show that the living poly(1) has a significantly lower nucleophilicity than that of styrene. It is obvious that the electron-withdrawing cyano group decreases the electron density of the terminal carbanion, resulting in the low nucleophilicity of living poly(1) as mentioned before.

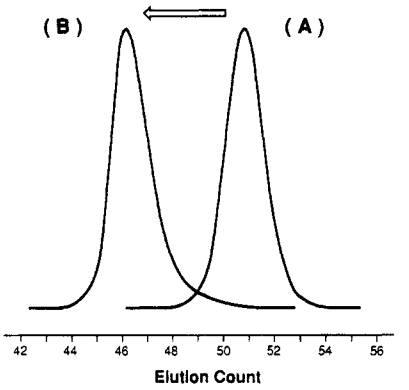


Figure 3. GPC curves of polystyrene at the first-stage polymerization (A) and of poly(1-*b*-styrene-*b*-1) obtained at −78 °C (B) (Table IV, run 35): peak A, $\bar{M}_n$(obsd) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.04; peak B, $\bar{M}_n$(obsd) = 21 000, $\bar{M}_w/\bar{M}_n$ = 1.07 (the second monomer was added 30 min after the first-stage polymerization).

With the use of more reactive methyl methacrylate (MMA) instead of styrene as the second monomer, MMA could be quantitatively initiated and polymerized by the propagating carbanion of living poly(1). The resulting triblock copolymer, poly(MMA-*b*-1-*b*-MMA), had a narrow MWD and predictable molecular weight as expected.

During our recent research, we have found similar phenomena in the anionic living polymerizations of a series of styrenes *para*-substituted with electron-withdrawing groups[2-7] (Chart I). In the anionic polymerization of these monomers, the lowered reactivities of the living polymers were similarly ascertained by the crossover reaction of the living carbanion and the various monomers. These stabilized carbanions may permit various styrene monomers containing electrophilic functionalities to undergo the living polymerization.

5. Some Physical Properties of Poly(cyanostyrene)s. The three poly(cyanostyrene)s obtained in this study were white powders and could be cast into transparent and brittle films from their solutions. Table V summarizes the solubilities of the resulting polymers and the block copolymer containing poly(1) segments. Some positional substituent effects on the solubilities of the polymers are observed. Poly(1) and poly(2) show similar solubilities in most solvents examined here. They are insoluble in nonpolar solvents such as benzene, carbon tetrachloride, diethyl ether, 1,4-dioxane, and ethyl acetate but soluble in polar solvents such as dimethyl sulfoxide, nitromethane, and acetonitrile. Chloroform and THF are useful solvents for poly(2) but they are ineffective for poly(1). The strong dipole moment or high polarity of the cyano group of both polymers may promote these solubilities, particularly in the polar solvents which cannot dissolve polystyrene. On the other hand, the solubility of poly(3) different from the solubilities of poly(1) and poly-

Table IV. Block Copolymerization of 1 with Styrene and Methyl Methacrylate at −78 °C in THF[a]

run	countercation	block sequence	A monomer	B monomer	block copolymer (homopolymer[b]) $10^{-3}\bar{M}_n$ calcd[c]	obsd[d]	$\bar{M}_w/\bar{M}_n$[e]
35	K^+	A–B–A	1	styrene	22 (12)	21 (12)	1.07 (1.04)
36[f]	K^+	A–B–A	1	styrene	23 (13)	25 (14)	1.09 (1.07)
37[g]	K^+	B–A–B	1	styrene	24 (9.4)	9.0[g] (9.0)	1.06[g] (1.06)
38	Li^+	B–A–B	1	MMA	25 (9.7)	26 (9.6)	1.11 (1.06)

[a] Yields of polymers were nearly quantitative in each case except for run 37. Difunctional initiators were used in all block copolymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + MW of initiator. [d] The molecular weights of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] $\bar{M}_w/\bar{M}_n$ was obtained by GPC calibration using standard polystyrenes in DMF solution. [f] After an end-capping of the difunctional living polystyrene with 1,1-diphenylethylene, block copolymerization was carried out by the addition of 1 in THF to the reaction mixture. [g] Homopoly(1) and unreacted sytrene monomer were quantitatively recovered from the reaction mixture.

Table V. Solubilities of Poly(cyanostyrene)s, Block Copolymer, and Polystyrene[a]

solvent	polymer poly(1)	poly(2)	poly(3)	block copolymer[b]	polystyrene
hexane	I	I	I	I	I
benzene	I	I	Sw	Sw	S
carbon tetrachloride	I	I	I	I	S
diethyl ether	I	I	S	I	S
ethyl acetate	I	I	Sw	Sw	S
chloroform	Sw	S	S	Sw	S
acetone	S	S	Sw	S	S
methyl ethyl ketone	S	S	Sw	S	S
1,4-dioxane	I	I	S	Sw	S
tetrahydrofuran	Sw	S	S	S	S
N,N-dimethylformamide	S	S	S	S	S
dimethyl sulfoxide	S	S	S	S	I
nitromethane	S	S	I	S	I
acetonitrile	S	S	I	I	I
ethanol	I	I	I	I	I
methanol	I	I	I	I	I
water	I	I	I	I	I

[a] I, insoluble; S, soluble; Sw, swelling. [b] Block copolymer of 1 and styrene shown in Table IV, run 35.

(2) but rather resembled with the solubility of polystyrene, although the molecular weight of poly(3) used here was only 6500 and the result was not very reliable. As expected, the block copolymer poly(1-*b*-styrene-*b*-1) shows solubilities intermediate between those of poly(1) and polystyrene.

Since we could synthesize poly(1)s with narrow MWDs, intrinsic viscosities of seven poly(1) samples were measured in DMF at 40 °C to estimate the physical property of poly(1) in solution. The [η] values and molecular weights of the polymer samples are shown in Table VI. It should be mentioned that these values are preliminary ones because the molecular weight range is rather limited for precise discussion. The plot of log [η] and log $\bar{M}_n$(NMR) gave a linear relationship in this molecular weight region as follows.

$$[\eta]_{DMF}^{40\,°C} = (1.004 \times 10^{-4})\bar{M}_n(\mathrm{NMR})^{0.749} \quad \text{for poly(1)}$$

The Mark–Houwink parameters, K and a, for poly(1) were hence estimated to be 1.00×10^{-4} and 0.75, respectively. The equation for polystyrene was also determined under the same conditions by using commercially available standard sample of $\bar{M}_n$ in the range $(5.11\text{–}294) \times 10^3$ with polydispersity indices of 1.01–1.04.[21]

$$[\eta]_{DMF}^{40\,°C} = (3.865 \times 10^{-4})\bar{M}_n^{0.582} \quad \text{for polystyrene}$$

The value of a for poly(1) is 0.75, indicating that DMF is a good solvent for poly(1). By contrast, the polymer chain of polystyrene ($a = 0.58$) contracted in DMF. These a values suggest that in DMF poly(1) has a larger hydrodynamic volume than polystyrene. This difference is accounted for by the higher polarity of poly(1) containing the cyano group than that of polystyrene. The molecular weights of poly(1)s are thereby always overestimated by using the polystyrene calibration of GPC measurements in DMF as shown in Table VI.

Table VI. Values of Intrinsic Viscosities and Molecular Weights for Poly(1)s

sample run	[η] (DMF 40 °C), dL/g	$10^{-3}\bar{M}_n$ obsd	GPC[a]	$\bar{M}_w/\bar{M}_n$
1	0.0902	8.7	23	1.07
2	0.121	13	33	1.07
3	0.155	20	45	1.07
4	0.242	30	80	1.04
5	0.257	33	94	1.05
6	0.338	61	140	1.06
7	0.663	122	270	1.09

[a] Molecular weights of poly(1)s were estimated by GPC calibration using standard polystyrenes in DMF at 40 °C.

Table VII. Glass Transition Temperatures of Poly(1)s[a]

$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g, °C	$10^{-3}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g, °C
8.7	1.07	161	30	1.04	179
13	1.07	158	61	1.06	179
14	1.07	157			
20	1.07	174	122	1.09	181

[a] Glass transition temperature was measured in the second heating scan at a rate of 20 °C/min.

The glass transition temperatures (T_gs) of the resulting poly(1)s were measured by differential scanning calorimety (DSC) (Table VII). Since the poly(1) samples used here had very narrow MWDs, they were suitable for the accurate discussion concenring T_g values. In fact, the molecular

weight dependence of T_g is clearly observed in the T_g measurement of poly(1). T_g increases with molecular weight of poly(1) and becomes constant at about 180 °C over the molecular weight of 30 000. This T_g of 180 °C is obviously higher than the reported T_g value of poly(4-cyanostyrene) obtained by free radical polymerization (T_g = 120 °C).[22] On the other hand, the T_gs of poly(2) and poly(3) could be measured to be 131 and 137 °C, respectively. The value for poly(3) is a preliminary one because its molecular weight is relatively low ($\bar{M}_n$ = 6500) for the estimation of T_g. However, these T_g values were lower than that of the *para* isomer but significantly higher than that of polystyrene (T_g = 101 °C) with nearly comparable molecular weight. The introduction of the polar cyano group into the aromatic ring may promote the higher T_gs of poly(cyanostyrene)s than that of polystyrene. Poly(1-*b*-styrene-*b*-1) show DSC peaks at 152 and 106 °C, corresponding to the T_gs of the poly(1) segment and the polystyrene block, respectively. Similarly, poly(MMA-*b*-1-*b*-MMA) exhibited T_gs at 169 and 113 °C, which were derived from the poly(1) and PMMA segment. These observations indicate that these triblock cause microphase separation in the bulk.

In conclusion, we have demonstrated the substituent effects on the anionic polymerizations of three cyanostyrenes. 4-Cyanostyrene is quantitatively polymerized with various anionic initiators to afford a stable living polymer. The living system leads to perfect control of the molecular weights and their distributions of the resulting polymers. On the other hand, the living polymerizations of 2- and 3-cyanostyrene are not achieved because of undesirable side reactions during the polymerization. The success of the living polymerization of 1 may be due to the stabilization of the growth center of the living poly(1) by the electron-withdrawing effect of the *para*-substituted cyano group.

Experimental Section

Materials. 4-Chlorostyrene, kindly supplied by Hokko Chemical Industry Co., Ltd., was used without further purification. *N*,*N*-Dimethylformamide was dried and distilled from calcium hydride under vacuum. Commercially available 3-bromoacetophenone, 2-bromobenzaldehyde, toluene, pyridine, and hydroxylamine hydrochloride were used without purification. 4-(Trimethylsilyl)chlorobenzene was synthesized by the Grignard reaction of 1,1-dichlorobenzene and trimethylsilyl chloride as previously reported.[10] Ethyl acetate was purified by standard techniques.[23] Styrene and α-methylstyrene were distilled over calcium hydride and finally distilled from benzylmagnesium chloride under vacuum. Methyl methacrylate was distilled over calcium hydride and finally distilled from triethylaluminum on the vacuum line.[24] 1,1-Diphenylethylene (DPE), prepared by a literature method,[25] was purified by fractional distillation and finally distilled from *n*-BuLi/heptane under vacuum. THF used as a polymerization solvent was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through a vacuum line from sodium naphthalenide solution.

Initiators. Commercially available *n*-butyllithium (1.6 M hexane solution) was diluted by *n*-heptane and used for the anionic polymerization. Metal naphthalenides were prepared by the reactions of a small excess molar quantity of naphthalene with the corresponding alkali metal in THF. Cumylpotassium was prepared by the reaction of cumyl methyl ether with sodium–potassium alloy in THF at room temperature. Oligo(α-methylstyryl)dilithium and -dipotassium were freshly prepared just prior to polymerizations from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. These initiators were stored at −30 °C in ampules equipped with breakseals. The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum.[26]

1,1-Bis[4′-(trimethylsilyl)phenyl]ethylene (4). 4-(Trimethylsilyl)chlorobenzene (16.2 g, 87.6 mmol) in dry THF (25 mL) was added dropwise over 30 min to a suspension of dry, clean magnesium turnings (3.19 g, 131 mmol) in dry THF (10 mL) at reflux temperature under nitrogen. After a further 8 h at reflux, the reaction mixture was cooled to 0 °C. Dry ethyl acetate (3.48 g, 39.5 mmol) was added dropwise to the reaction mixture with cooling in an ice bath, and the mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and concentrated under reduced pressure.

To the residue was added 20% H_2SO_4 (26 mL), and the resulting mixture was heated at reflux for 2 h. The reaction mixture was cooled to room temperature to give a yellow solid. The solid was taken up in ether (100 mL), and the solution was washed twice with water, five times with saturated $NaHCO_3$ solution, and twice with water. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a slightly yellow solid (9.42 g, 74%). The solid was recrystallized from methanol three times to yield a pure white crystal of 4 (3.77 g, 11.6 mmol, 29%): mp 112.0–113.0 °C; 90-MHz ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 18H, $SiCH_3$), 5.48 (s, 2H, CH_2=), 7.37–7.55 (m, 8H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ −1.0 ($SiCH_3$), 114.0 (CH_2=), 127.7 (Ar, C2), 133.3 (Ar, C3), 139.9 (Ar, C1), 141.9 (Ar, C4), 150.2 (-C=); IR (KBr, cm^{-1}) 2955, 1247, 1118, 1085, 914, 857, 831, 753, 727. Anal. Calcd for $C_{20}H_{28}Si_2$: C, 74.00; H, 8.69. Found: C, 73.82; H, 8.90.

After careful recrystallization, 4 was finally distilled from *n*-BuLi/pentane in an apparatus equipped with a breakseal under high vacuum and then diluted with dry THF. The resulting THF solution (0.05 M) of 4 was used in the anionic polymerization.

3-Bromostyrene.[27] To a solution of $NaBH_4$ (2.45 g, 64.7 mmol) in ethanol (130 mL) was added 3-bromoacetophenone (25.83 g, 130 mmol) dropwise under cooling in an ice bath. After stirring for 2 h at room temperature, the reaction mixture was poured into could 2 N HCl (100 mL) and extracted three times with diethyl ether. The organic layer was washed with saturated $NaHCO_3$ solution and brine and then dried over anhydrous $MgSO_4$. The organic phase was combined and concentrated under reduced pressure to give a rough (3-bromophenyl)methylcarbinol.

To a heated mixture of $KHSO_4$ (2.98 g, 21.9 mmol) and 4-*tert*-butylcatechol (10 mg) at 230 °C under reduced pressure (120 mmHg), the carbinol was added dropwise over 1 h. The carbinol was immediately dehydrated and the product was azeotropically distilled through the condenser. The distillate was extracted three times with diethyl ether and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 3-bromostyrene (12.67 g, 69 mmol, 53%, bp 31–32 °C/0.5 mmHg): 90-MHz ^{1}H NMR ($CDCl_3$) δ 5.29 and 5.72 (2 d, 2H, J = 11 and 18 Hz, CH_2=), 6.68 (dd, 1H, -CH=), 7.08–7.55 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 115.3 (vinyl, CH_2=), 122.8 (Ar, C3), 124.9 (Ar, C6), 129.1 (Ar, C2), 130.0 (Ar, C5), 130.6 (Ar, C4), 135.5 (vinyl, -CH=), 139.7 (Ar, C1).

2-Bromostyrene.[27] To a mixture of methyltriphenylphosphonium bromide (51.1 g, 143 mmol) and potassium *tert*-butoxide (28.7 g, 255 mmol), 120 mL of dry THF was added at room temperature under nitrogen. To the mixture under cooling in an ice bath, 2-bromobenzaldehyde (24.96 g, 135 mmol) was added dropwise over 30 min. After stirring for 1 h at 0 °C, the reaction mixture was quenched with water (150 mL), and the layers were separated. The aqueous layer was extracted three times with dichloromethane. The combined organic phase was concentrated by evaporation and poured into diethyl ether to precipitate triphenylphosphine oxide. After filtration, the filtrate was concentrated and purified by flash chromatography (petroleum ether). After concentration of the effluent, the residue was distilled under vacuum to give a colorless liquid of 2-bromostyrene (17.50 g, 96 mmol, 71%, bp 57–58 °C/6 mmHg): 90-MHz ^{1}H NMR ($CDCl_3$) δ 5.36 and 5.69 (2 d, 2H, J = 11 and 17 Hz, CH_2=), 7.10 (dd, 1H, -CH=), 7.09–7.59 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 116.7 (vinyl, CH_2=), 123.7 (Ar, C2), 126.9 (Ar, C5), 127.5 (Ar, C6), 129.1 (Ar, C4), 132.9 (Ar, C3), 135.9 (vinyl, -CH=), 137.6 (Ar, C1).

4-Formylstyrene.[28] To a suspension of dry, clean magnesium turnings (8.42 g, 347 mmol) in dry THF (50 mL) at reflux temperature under nitrogen, 4-chlorostyrene (31.84 g, 230 mmol) in dry THF (150 mL) was added dropwise over 30 min. After a further 30 min at reflux, the reaction mixture was cooled to 0 °C. To the reaction mixture, dry DMF (21.20 g, 290 mmol) was added dropwise with cooling in an ice bath, and the mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 4-formylstyrene (25.71 g, 195 mmol, 85%, bp 55–57 °C/0.5 mmHg): 90-MHz ^1H NMR ($CDCl_3$) δ 5.43 and 5.90 (2 d, 2H, J = 11 and 18 Hz, $=CH_2$), 6.78 (dd, 1H, $-CH=$), 7.71 (m, 4H, aromatic), 9.98 (s, 1H, CHO); 23-MHz ^{13}C NMR ($CDCl_3$) δ 117.2 (vinyl, $=CH_2$), 126.7 (Ar, C2), 130.0 (Ar, C3), 135.9 (vinyl, $-CH=$), 138.0 (Ar, C4), 143.5 (Ar, C1), 191.6 (CHO).

3-Formylstyrene.[28a] All our attempts to synthesize 3-formylstyrene from the Grignard reaction between 3-chlorostyrene and DMF were unsuccessful. The Grignard reagent of 3-chlorostyrene showed a high tendency to spontaneously polymerize as reported previously.[28a] Even Rieke's method[29] using the highly activated magnesium gave quantitatively insoluble polymer. We hence utilized 3-bromostyrene for the synthesis of 3-formylstyrene by way of the organomagnesium reagent.

To a suspension of dry, clean magnesium turnings (5.96 g, 245 mmol) in dry THF (120 mL) under cooling in an ice bath under nitrogen, 3-bromostyrene (29.56 g, 162 mmol) in dry THF (40 mL) was added dropwise over 30 min. Stirring was continued for 2 h at room temperature. To the reaction mixture, dry DMF (30.56 g, 419 mmol) was added dropwise at 0 °C, and the mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with saturated ammonium chloride solution, and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was washed with saturated $NaHCO_3$ solution and with brine and then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled under vacuum to give a colorless liquid of 3-formylstyrene (16.10 g, 122 mmol, 75%, bp 47–49 °C/0.5 mmHg (lit.[28a] bp 74–78 °C/1 mmHg)): 90-MHz ^1H NMR ($CDCl_3$) δ 5.37 and 5.85 (2 d, 2H, J = 11 and 17 Hz, $CH_2=$), 6.80 (dd, 1H, $-CH=$), 7.49–7.91 (m, 4H, aromatic), 10.03 (s, 1H, CHO); 23-MHz ^{13}C NMR ($CDCl_3$) δ 115.7 (vinyl, $CH_2=$), 127.1 (Ar, C2), 128.9, 129.2, and 131.9 (Ar, C4, C5, and C6), 135.6 (vinyl, $-CH=$), 136.7 (Ar, C3), 138.5 (Ar, C1), 192.1 (CHO).

2-Formylstyrene.[28a] A procedure similar to that described above for 3-formylstyrene was followed using magnesium (3.12 g, 130 mmol), DMF (19.43 g, 266 mmol), and 2-bromostyrene (16.08 g, 88 mmol) in place of 3-bromostyrene. Distillation in vacuo gave 9.35 g (71 mmol, 85%, bp 61.5–62.0 °C/0.5 mmHg (lit.[28a] bp 113–115 °C/18 mmHg)) of 2-formylstyrene as a colorless liquid: 90-MHz ^1H NMR ($CDCl_3$) δ 5.49 and 5.67 (2 d, 2H, J = 11 and 17 Hz, $CH_2=$), 7.30–7.86 (m, 5H, aromatic and $-CH=$), 10.26 (s, 1H, CHO); 23-MHz ^{13}C NMR ($CDCl_3$) δ 119.2 (vinyl, $CH_2=$), 132.9 (Ar, C2), 133.7 (vinyl, $-CH=$), 127.3, 127.9, 131.1, and 133.3 (Ar, C3, C4, C5, and C6), 140.4 (Ar, C1), 192.2 (CHO).

4-Cyanostyrene (1)[11] was prepared by the modified method according to the procedure reported by Saednya.[13] To a mixture of hydroxylamine hydrochloride (13.91 g, 200 mmol), pyridine (31.60 g, 400 mmol), and 4-*tert*-butylcatechol (10 mg) was added 4-formylstyrene (25.74 g, 195 mmol) in one portion at room temperature. After 3–5 min of stirring, toluene (200 mL) was added, and the mixture was heated for 10 h under reflux with azeotropic separation of water by means of a Dean–Stark water trap. The cooled solution was filtered from pyridinium chloride. The filtrate was washed twice with 1 N HCl, twice with saturated $NaHSO_3$ solution, and twice with H_2O and dried over anhydrous $MgSO_4$. After removal of toluene under vacuum, distillation gave 17.24 g (134 mmol, 69%) of 1 as a colorless liquid at 56–58 °C/0.3 mmHg (lit.[11a] bp 102–104 °C/9 mmHg): 90-MHz ^1H NMR ($CDCl_3$) δ 5.45 and 5.87 (2 d, 2H, J = 11 and 18 Hz, $CH_2=$), 6.75 (dd, 1 H, $-CH=$), 7.43–7.68 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 110.9 (Ar, C4), 117.6 (vinyl, $CH_2=$), 118.7 (CN), 126.6 (Ar, C2), 132.2 (Ar, C3), 135.2 (vinyl, $-CH=$), 141.8 (Ar, C1); IR (KBr, cm^{-1}) 2228 (CN), 1629, 1606, 1506, 1406, 1285, 1176, 1116, 990, 923, 847. Anal. Calcd for C_9H_7N: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.29; H, 5.49; N, 10.81.

3-Cyanostyrene (2).[30] The same procedure was followed as described above for 1 using hydroxylamine hydrochloride (8.55 g, 123 mmol), pyridine (19.5 mL, 244 mmol), toluene (150 mL), and 3-formylstyrene (16.10 g, 122 mmol) in place of 4-formylstyrene. Distillation in vacuo gave 11.36 g (88.1 mmol, 72%, bp 33–34 °C/0.3 mmHg (lit.[30] bp 83 °C/3.5 mmHg)) of 2 as a colorless liquid: 90-MHz ^1H NMR ($CDCl_3$) δ 5.41 and 5.78 (2 d, 2H, J = 11 and 18 Hz, $CH_2=$), 6.73 (dd, 1H, $-CH=$), 7.27–7.68 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 112.7 (Ar, C3), 116.5 (vinyl, $CH_2=$), 118.5 (CN), 129.3 (Ar, C5), 129.6 (Ar, C6), 130.2 (Ar, C2), 130.9 (Ar, C4), 134.7 (vinyl, $-CH=$), 138.6 (Ar, C1); IR (KBr, cm^{-1}) 2231 (CN), 1635, 1598, 1577, 1479, 1397, 1280, 990, 920, 897, 802. Anal. Calcd for C_9H_7N: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.07; H, 5.93; N, 10.76.

2-Cyanostyrene (3).[31] The same procedure was followed as described above for 1 using hydroxylamine hydrochloride (5.31 g, 76.4 mmol), pyridine (13.0 mL, 165 mmol), toluene (120 mL), and 2-formylstyrene (9.35 g, 70.8 mmol) in place of 4-formylstyrene. Distillation in vacuo gave 5.50 g of 3 (42.6 mmol, 60%, bp 42–43 °C/0.4 mmHg (lit.[31] bp 53 °C/0.15 mmHg)) as a colorless liquid: 90-MHz ^1H NMR ($CDCl_3$) δ 5.52 and 5.92 (2 d, 2H, J = 11 and 18 Hz, $CH_2=$), 7.09 (dd, 1H, $-CH=$), 7.25–7.72 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 110.9 (Ar, C2), 117.5 (CN), 118.7 (vinyl, $CH_2=$), 125.3, 127.8, 128.9, and 131.9 (Ar, C3, C4, C5, and C6), 132.6 (vinyl, $-CH=$), 140.4 (Ar, C1); IR (KBr, cm^{-1}) 2226 (CN), 1630, 1598, 1566, 1479, 1450, 1286, 1210, 985, 927, 772, 754. Anal. Calcd for C_9H_7N: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.39; H, 5.42; N, 10.73.

Monomer Purification. After careful fractional distillation, the purified cyanostyrenes were sealed off under a degassed condition in an apparatus equipped with a breakseal in the presence of CaH_2. The monomer was stirred for 24 h at ambient temperature and then distilled from CaH_2 on a vacuum line into ampules fitted with breakseals. Next, to remove impurities in the monomer, phenylmagnesium chloride (5.0 mL, 0.20 M solution in THF) was added to the monomer (5.88 g, 46 mmol) at −78 °C under vacuum (10^{-6} mmHg), and the mixture was stirred for 30 min at ambient temperature. It was distilled again under vacuum into the apparatus equipped with breakseals and diluted with dry THF. The resulting monomer solutions (0.3–0.5 M in THF) were stored at −30 °C until ready to use for the anionic polymerization.

Polymerization Procedures. All polymerizations were carried out at low temperature with shaking under high-vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[26] The polymerization reaction was quenched with methanol. The reaction mixture was dissolved by the addition of DMF and then poured into a large excess of methanol to precipitate the polymer. Polymers collected by filtration were purified by reprecipitation twice with either a methanol–DMF (for poly(1)) and a methanol–THF (for poly(2) and poly(3)) system. Polymers thus obtained were characterized by ^1H and ^{13}C NMR, IR spectroscopy, and elemental analysis. The following is the full list.

Poly(4-cyanostyrene): 90-MHz ^1H NMR (DMF-d_7) δ 1.4–2.5 (m, 3H, CH_2CH), 6.7–7.7 (m, 4H, aromatic); 23-MHz ^{13}C NMR (DMF-d_7) δ 40–44 (m, CH_2CH), 109.8 (Ar, C4), 119.2 (CN), 129.2 (Ar, C2), 132.6 (Ar, C3), 150.5 (Ar, C1); IR (KBr, cm^{-1}) 2228 (CN), 1672, 1607, 1505, 1453, 1416, 1177, 1018, 836. Anal. Calcd for $(C_9H_7N{\cdot}0.2H_2O)_n$: C, 81.42; H, 5.62; N, 10.55. Found: C, 81.60; H, 5.34; N, 10.90.

Poly(3-cyanostyrene): 90-MHz ^1H NMR ($CDCl_3$) δ 0.6–2.7 (m, 3H, CH_2CH), 6.2–7.9 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 40–45 (m, CH_2CH), 112.7 (Ar, C3), 118.3 (CN), 128–133 (Ar, C2, C4, C5, C6), 145 (Ar, C4); IR (KBr, cm^{-1}) 2928, 2229 (CN), 1601, 1582, 1482, 1433, 1248, 896, 848, 797. Anal. Calcd for $(C_9H_7N{\cdot}0.1H_2O)_n$: C, 82.54; H, 5.54; N, 10.70. Found: C, 82.38; H, 5.72; N, 9.59.

Poly(2-cyanostyrene): 90-MHz ^1H NMR ($CDCl_3$) δ 1.2–3.0 (m, 3H, CH_2CH), 6.5–7.9 (m, 4H, aromatic); 23-MHz ^{13}C NMR ($CDCl_3$) δ 40–43 (m, CH_2CH), 112 (Ar, C2), 118 (CN), 125–128, 133, 147 (Ar, C1); IR (KBr, cm^{-1}) 2931, 2223 (CN), 1599, 1574, 1526, 1484, 1448, 1336, 1163, 1031, 759. Anal. Calcd for

$(C_9H_7N\cdot 0.2H_2O)_n$: C, 81.42; H, 5.62; N, 10.55. Found: C, 81.87; H, 5.62; N, 9.58.

Postpolymerization. In the all-glass apparatus in vacuo, the first-stage polymerization of 1 was carried out with (1,1,4,4-tetraphenylbutanediyl)dilithium as an initiator in THF at −78 °C for 30 min. After sampling to determine the characteristics of the first-stage polymer, to the residual polymerization system, the second feed of 1 was added and reacted for 30 min to complete the further polymerization. After quenching with methanol, both pre- and postpolymer of 1 were quantitatively obtained. Both polymers possessed narrow MWDs and predictable molecular weights, as expected. With use of potassium initiator (cumylpotassium capped with 1,1-diphenylethylene), a similar result was obtained.[10] Block copolymerizations of 1 were performed in a similar manner.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C) in $CDCl_3$ or DMF-d_7. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0.00) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Chemical shifts of poly(1) were reported in ppm downfield relative to DMF-d_7 (δ 8.05) for ^1H NMR and (δ 162.5) for ^{13}C NMR as standard. Gel permeation chromatograms (GPC) for MWD determinations of polymers were obtained at 40 °C with a TOSOH HCL-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H_{XL}, G4000H_{XL}, and G3000H_{XL}) with ultraviolet (270 nm in DMF or 254 nm in THF) or refractive index detection. DMF (for poly(1)) or THF (for poly(2) and poly(3)) was the carrier solvent at a flow rate of 1.0 mL min^{-1}. Laser light scattering (LS) measurements for weight-average molecular weight determination of poly(1) were performed at 25 °C with an Ootsuka Electronics DSL-600R instrument in DMF solution. Intrinsic viscosities of poly(1) and polystyrene were measured by using an Ubbelohde type capillary viscometer at 40 °C in DMF. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 240 °C, cooled rapidly to −20 °C, and then scanned again at a rate of 20 °C min^{-1}.

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